Field volatility of Dicamba DGA

Report:	MRID 50102118. Mitchell, J., Grant, S., and Ghebremichael, L. 2017. Dicamba. Dicamba-S-Metolachlor Herbicide Formulation Containing Vapor Grip (A21472C) - Volatility of Dicamba In A21472C When Applied Post-Emerge to a Soybean Crop in the Midwestern United States. Final Report. Unpublished study performed by Waterborne Environmental, Inc., Leesburg, Virginia; Syngenta Crop Protection, LLC, Greensboro, North Carolina; and SynTech Research Laboratories, LLC, Stilwell, Kansas. Sponsored by Syngenta Crop Protection, LLC, Greensboro, North Carolina. Report No. & Waterborne Study No.: 796.128. Syngenta Study No. & Task No.: TK0281284. SynTech Study No.: 069SRUS16R175. Study initiation July 8, 2016 and completion February 28, 2017 (p. 7). Final report issued February 28, 2017.
Document No.:	MRID 50102118
Guideline:	OCSPP 835.8100
Statements:	The study was conducted in compliance with US EPA FIFRA GLP standards (40 CFR Part 160) with the following exceptions (p. 3): 1) Test site information such as subsurface drainage, estimation of the slope, depth to water, elevation, and GPS coordinates 2) Study weather data 3) Pesticide and crop histories for the test plot 4) Soil information 5) Test plot preparation and maintenance and pesticide maintenance applications 6) Documentation regarding the preparation of transit stability and field exposed quality control samples was added after preparation 7) The location of frozen storage of QC samples prior to shipment was not documented in the raw data Signed and dated Data Confidentiality, GLP Compliance, and Quality Assurance statements were provided (pp. 2-5). No Authenticity Certification statement is provided.
Classification:	This study is **acceptable**. Dicamba was detected in two pre-application samples, but this does not appear to have affected the results. Laboratory spiked samples show that there was poor recovery (*i.e.*,74-89%) at lower measurement levels (*i.e.*, 2 ng/sample), indicating the method may have not been adequate at concentrations near the LOQ. The minimum fetch required for use of the aerodynamic method was not satisfied for all samplers, so this method was not assessed.
PC Code:	128931
Final EPA Reviewer:	Chuck Peck Senior Scientist Signature: Date: 2019.04.08 07:08:34 -04'00'
CDM/CSS-Dynamac JV Reviewers:	Richard Lester Environmental Scientist Signature: Date: 11/28/17

Kathleen Ferguson, Ph.D.,
Environmental Scientist

Signature: Kathleen P. Ferguson
Date: 11/28/17

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel.

Executive Summary

Field volatilization of dicamba in A21472C Herbicide with VaporGrip™ Technology, was examined from cropped plots at two plots in York County, Nebraska. The site(s) where the studies were conducted were *ca*. 7 miles west northwest of York, Nebraska. The experiments were conducted for seven days. The nominal application rate for dicamba in both plots was 0.5 lbs. a.e./A. The treated plots were 1,000 feet (305 m) apart. Applications were conducted two days apart on July 12 and 14, 2016. Application methods were identical for the two plots.

Under field conditions at Plot FV1, based on calculations using the Integrated Horizontal Flux method, dicamba had a peak volatile flux rate of 0.572 ng/m^2·s accounting for 0.022% of the applied mass observed 15.6 to 21.6 hours post-application. By the end of the study, a total of 0.05% of dicamba volatilized and was lost from the field. Observed flux rates were diurnal and generally highest during daytime periods of high temperatures, except for the highest flux rate which occurred between 1 and 7 am.

Under field conditions at Plot FV2, based on calculations using the Integrated Horizontal Flux method, dicamba had a peak volatile flux rate of 1.01 ng/m^2·s accounting for 0.0128% of the applied mass observed 0 to 1.97 hours post-application. By the end of the study, a total of 0.045% of dicamba volatilized and was lost from the field. Observed flux rates were diurnal and generally highest during daytime periods of high temperatures.

Figure 1. Estimated flux rate – Plot FV1

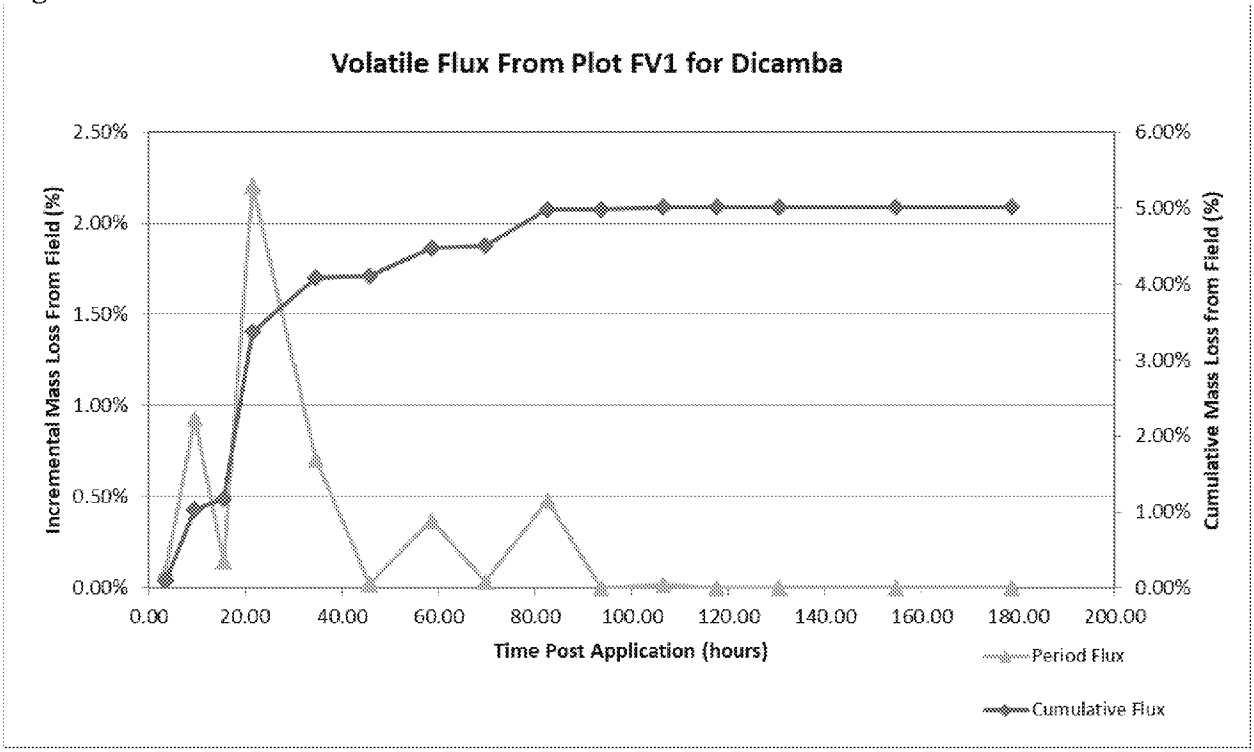
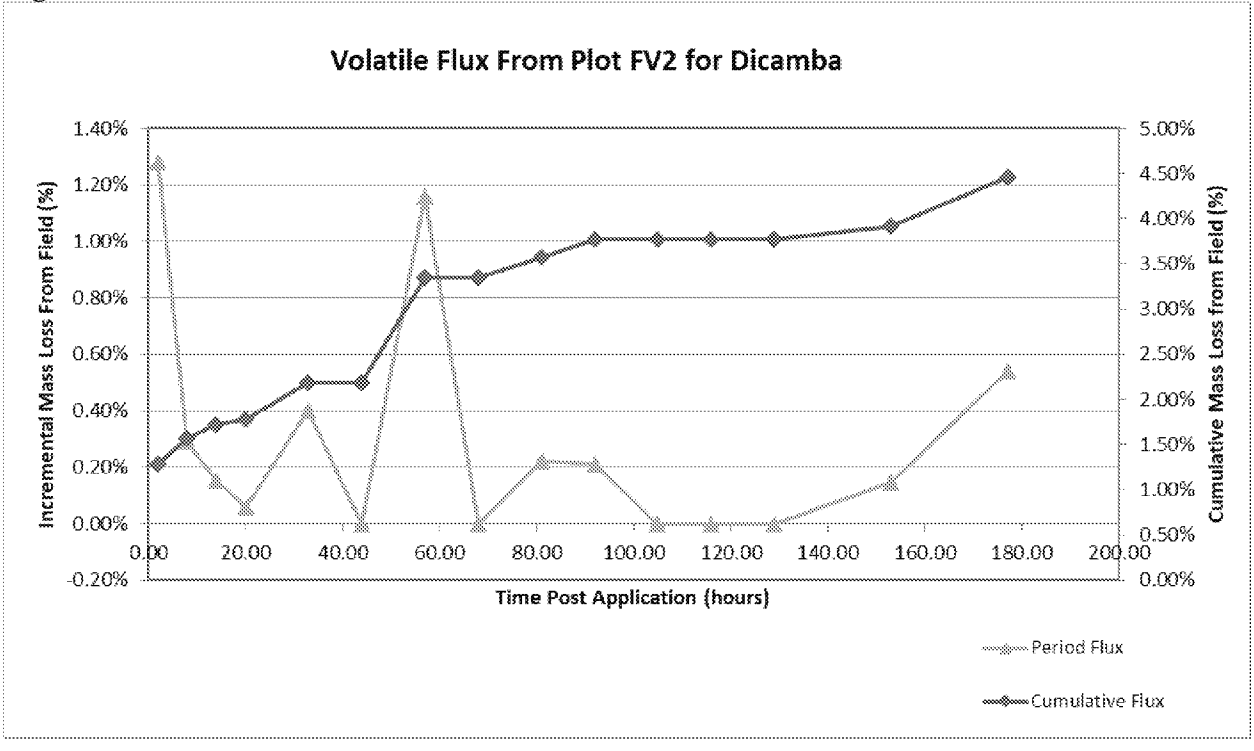


Figure 2. Estimated flux rate – Plot FV2



I. Materials and Methods

A. Materials

1. Test Material

Product Name: A21472C Herbicide
with VaporGrip™ Technology (Table 7, p. 45)
Formulation Type: Liquid
CAS #: 1918-00-9 (for dicamba; p. 16)
Storage stability: The expiration date of the test substance was July 31, 2019 (Table 7, p. 45). No further stability or degradation information is provided for the test substance.

2. Storage Conditions

The test material was received on June 27 and July 14, 2016. The material was stored in a chemical storage building at ambient temperatures of 70°F to 84°F (21°C to 29°C) prior to final application on July 14, 2016 (p. 15).

B. Study Design

1. Site Description

The test site was located on agricultural land near York, Nebraska (p. 16). Two 9.4-acre (3.8 ha) soybean plots were treated *ca.* 30 days post-emergence (pp. 17-18). The plot dimensions were 640 feet × 640 feet (195 m × 195 m). Soil was classified as a Hastings silt loam, a very deep, well-drained soil that formed in loess dominantly from interfluves and hill slopes on loess uplands. The taxonomic class is fine, smectitic, mesic Udic Argiustolls (Order – Mollisols, Suborder – Ustolls). The crops on both plots for the previous three years were sorghum and soybean (2013), soybean (2014), and sorghum (2015; Table 8, p. 46). Pesticides applied during the previous three years were Lariat, Glyphosate, Select, 2,4-D, Boundary, Volunteer, Volley XT, Atrazine, and Clarity. The plots were separated by *ca.* 1,000 feet (305 m; Figure 9, p. 61). The elevation of the site was *ca.* 1,707 feet above sea level, and the slope in the area was estimated to be less than 1%.

2. Application Details

Application rate(s): The target application rate was 0.5 lb a.e./A (0.561 kg a.e./ha) for dicamba and 1 lb a.i./A (1.12 kg a.i./ha) for S-metolachlor (p. 18). Application monitoring samples were collected from ten locations on each plot using pans containing filter papers (p. 29). Application monitoring indicated that application was within 6.59% of the theoretical target value at plot FV1 and within 0.95% of the theoretical target value at plot FV2.

Irrigation and Water Seal(s): No irrigation water was used during the study period (p. 17).

Tarp Applications: Tarps were not used.

Application Equipment: A Hagie boom sprayer was used for broadcast application at both plots (p. 19). The spray boom was fitted with 32 flat fan Turbo Teejet® Induction (TTI) 11004 nozzles and 50 mesh screens. Nozzles were evenly spaced 30 inches apart, providing an 80-foot swath width. The boom height was set *ca.* 30 inches above the soybean canopy. The sprayer was equipped with a 400-gallon tank, and a centrifugal pump was used to pressurize the system and provide agitation (recirculation). A paddle wheel also provided agitation.

Equipment Calibration Procedures: The sprayer output at each application was calibrated using water, and the spray from each nozzle was collected for 30 seconds (p. 19). The boom pressure was set at 33 psi for all calibration trials and test substance applications. The calibrated sprayer outputs were 14.4 GPA for the FV1 application and 15.2 GPA for the FV2 application. The target sprayer speeds were 7.31 and 7.28 feet/sec (4.99 and 4.96 mph), respectively (Table 11, p. 49).

Application Regime: The application rates and methods used in the study are summarized in **Table 1**.

Table 1. Summary of application methods and rates for A21472C.

Plot	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied (lbs)	Area Treated (acres)	Target Application Rate (lb ae/acre)	Reported Application Rate (gal/acre)
FV1	Broadcast Spray	7/12/2016 8:53	4.7[1]	9.4	0.5	14.4
FV2	Broadcast Spray	7/14/2016 10:30	4.7[1]	9.4	0.5	15.2

Data obtained from pp. 18-19; and Tables 11-12, pp. 49-50, of the study report.
[1] Reviewer calculated as area treated (9.4 acres) × target application rate (0.5 lb ae/acre).

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

Table 2. Summary of A21472C application and monitoring schedule.

Plot	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
FV1	9.4	7/12/16 between 8:53 – 9:23	7/12/16 between 9:24 – 13:00	Not Applicable	Not Applicable
FV2	9.4	7/14/16 between 10:30 – 11:02	7/14/16 between 11:02 – 13:00	Not Applicable	Not Applicable

Data obtained from p. 19 and Tables 12-13, pp. 50-51, of the study report.

3. Soil Properties

Soil properties measured before the study are provided in **Table 3**.

Table 3. Summary of soil properties for fields/plots.

Field	Sampling Depth	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm^3)	Soil Composition
FV1	0-6 inches	Silt Loam	Hastings Silt Loam	Fine, smectic, mesic Udic Argiustoll (Order – Mollisols, Suborder – Ustolls)	1.06	% Organic Carbon[1] = 1.69% % Sand = 20% %Silt = 58% %Clay = 22% pH = 6.6
FV2	0-6 inches	Silt Loam	Hastings Silt Loam	Fine, smectic, mesic Udic Argiustoll (Order – Mollisols, Suborder – Ustolls)	1.06	% Organic Carbon[1] = 1.74% % Sand = 20% %Silt = 56% %Clay = 24% pH = 6.1

Data obtained from p. 17 and Table 9, p. 47, of the study report.
[1]Reviewer calculated as: organic carbon (%) = organic matter (%) / 1.72. Organic matter was reported as 2.9% for FV1 and 3.0% for FV2.

Figures 3 and **4** present plots of soil temperature (°C) and soil volumetric water content at depths of 2 inches and 6 inches measured throughout the study (Appendix 4, pp. 99-103).

Figure 3. Soil temperature (°C) throughout the study.

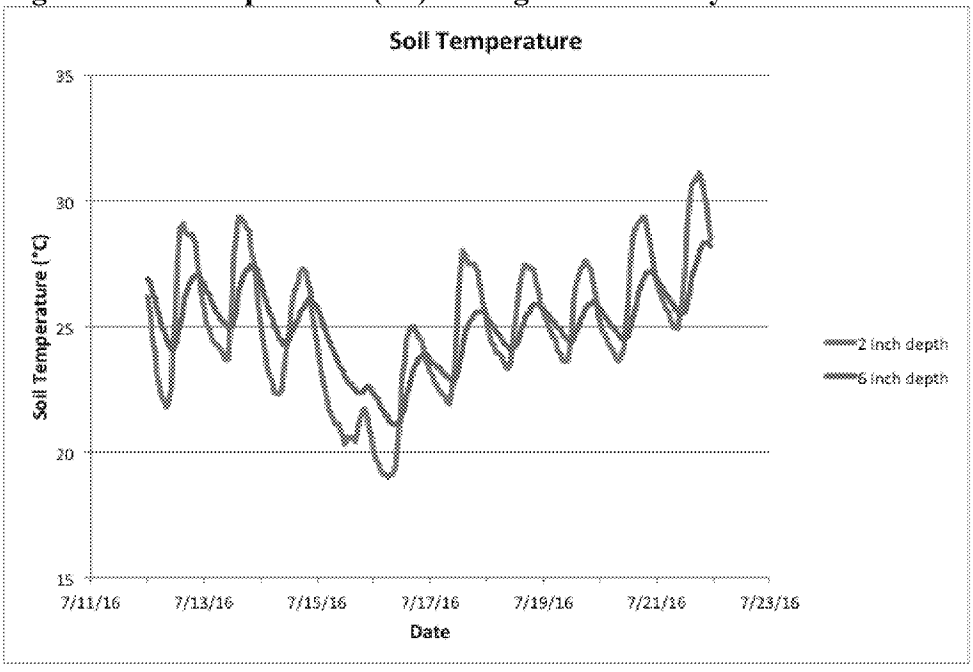
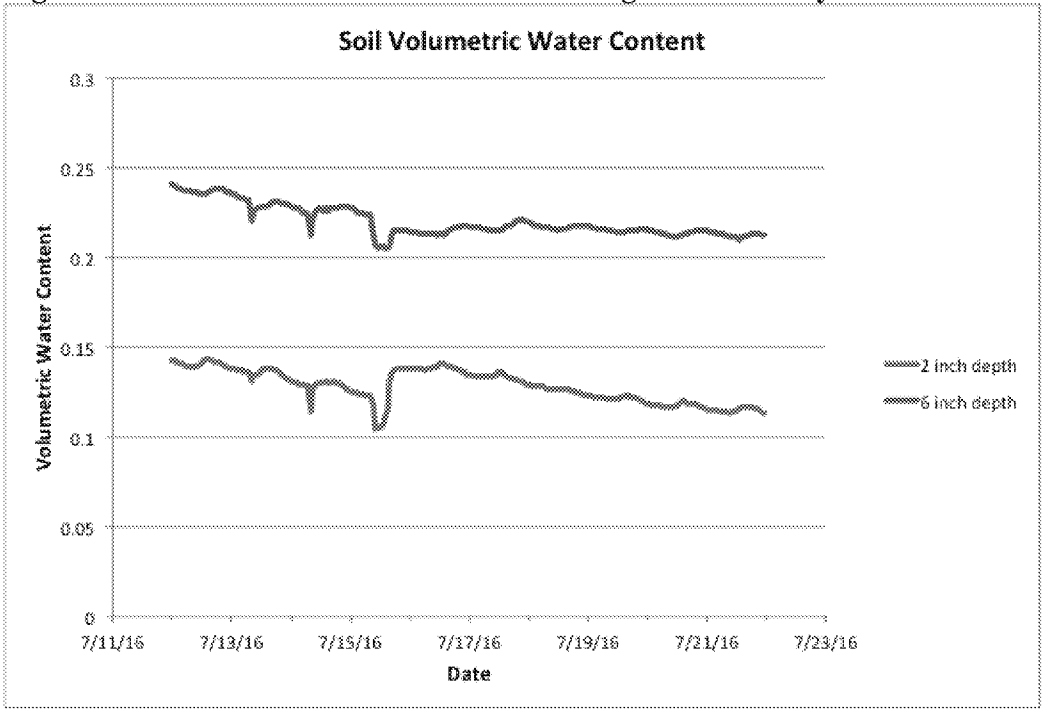


Figure 4. Soil volumetric water content throughout the study.



4. Meteorological Sampling

Air temperature, wind speed, and wind direction were measured at a flux meteorological station within *ca.* 5 meters of each plot (p. 18). Measurements were made every second and summarized every minute and every hour for the duration of the experiment at heights of 0.15, 0.33, 0.55, 0.90, and 1.5 meters above the soybean canopy. A standard weather station was located midway between the two plots and measured hourly air temperature, soil temperature, precipitation, relative humidity, wind speed and direction, barometric pressure, reference evapotranspiration, and solar radiation data at a height of 2 meters above the canopy. Additional precipitation data were collected from a manual rain gauge. One-minute solar radiation data were also recorded during application.

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in **Table 4**. The location of the meteorological equipment for each field is shown in **Attachment 3**.

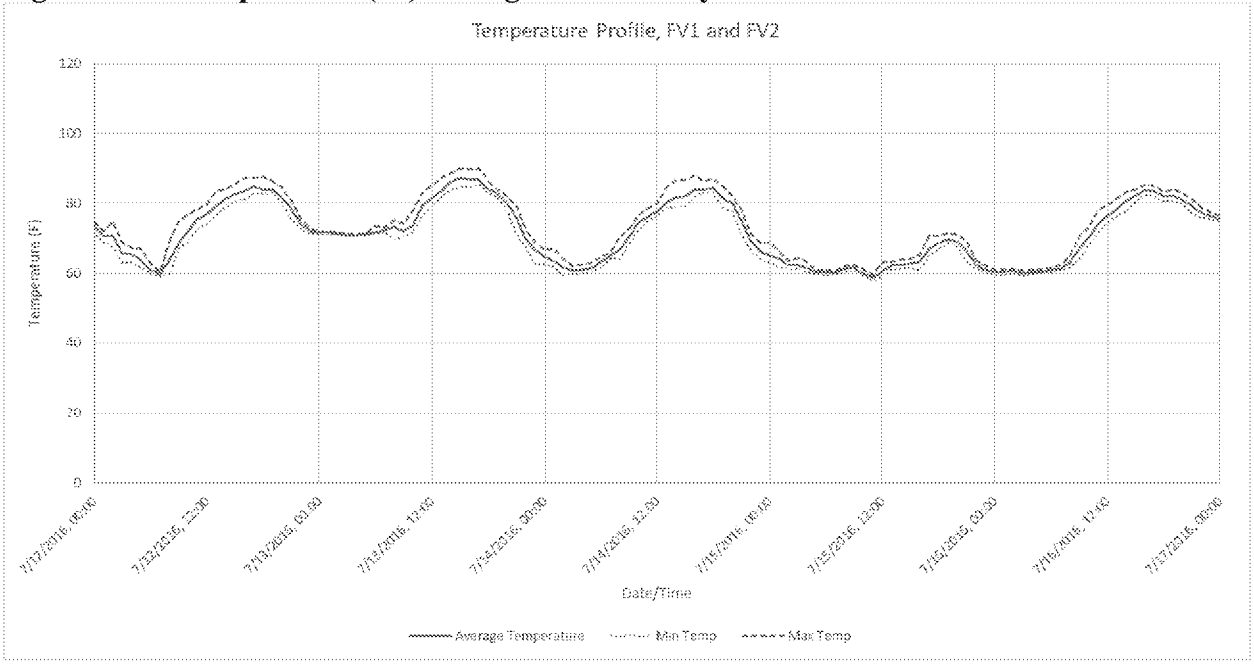
Table 4. Summary of meteorological parameters measured in the field.

Plot	Minimum Fetch (m)	Parameter	Monitoring heights (m)	Averaging Period
FV1	97.7	Wind speed/Wind direction	0.15, 0.33, 0.55, 0.90, 1.5	1 minute
		Ambient air temperature	0.15, 0.33, 0.55, 0.90, 1.5	1 minute
FV2	97.6	Wind speed/Wind direction	0.15, 0.33, 0.55, 0.90, 1.5	1 minute
		Ambient air temperature	0.15, 0.33, 0.55, 0.90, 1.5	1 minute
Between FV1 & FV2	Not Applicable	Ambient air temperature	2	1 hour
		Soil temperature	2-inch depth, 6-inch depth	1 hour
		Precipitation	2	1 hour
		Relative humidity	2	1 hour
		Wind speed/Wind direction	2	1 hour
		Barometric pressure	2	1 hour
		Reference evapotranspiration	2	1 hour
		Solar radiation	2	1 hour

Data obtained from p. 18; Appendix 7, p. 117; and Appendix 11, p. 132 of the study report.

Figure 5 depicts the air temperature during the conduct of the study. The maximum instantaneous temperature for FV1 occurred the day after the application and was 90°F. Average hourly temperatures on the first three days ranged from 60-87°F. The maximum instantaneous temperature for FV2 occurred the day of the application and was 88°F. Average hourly temperatures on the first three days ranged from 59-84°F. Temperatures followed a diurnal and nocturnal pattern, with highs occurring during the day and lows occurring at night. The relative humidity for FV1 ranged from 23 to 100% 0 to 2 DAT. The relative humidity for FV2 ranged from 28 to 100% 0 to 2 DAT.

Figure 5. Air temperature (°F) throughout the study.



5. Air Sampling

Eight off-field air monitoring stations were utilized to determine the concentration of dicamba in air during application (p. 20). These stations were located *ca.* 10 meters from each corner and the center of each edge of the plot. The sampling height was 1.5 meters above the soybean canopy.

Following application completion, air samples were collected from an on-field monitoring station located in the center of each plot (p. 20). Air sampling pumps were mounted on a sampling mast at heights of *ca.* 0.15, 0.33, 0.55, 0.90, and 1.5 meters above the soybean canopy.

Pre-application samples were collected at the on-field air monitoring location in the center of each plot at heights of 0.15 and 0.33 meters for *ca.* 24 hours prior to the start of each application (p. 21).

6. Sample Handling and Storage Stability

Upon collection, the polyurethane foam (PUF) tubes were individually sealed in plastic bags, labeled, and placed in an ice chest with ice packs until they were transported to a freezer (p. 20). The air samples were shipped via freezer truck to SynTech Research Laboratories, LLC for analysis (p. 21). Freezer temperatures during storage were monitored daily and ranged from -12 to -16°F (-24 to -27°C; p. 22). The maximum storage interval from collection to initial extraction for PUF tubes was 115 days (Appendix 14, p. 279). Freezer storage stability experiment results indicated average dicamba recovery of 101% ± 3.4% at day 90 in samples fortified at 100x LOQ (p. 34). Transit stability results at 1000X LOQ indicated dicamba recoveries of 91% ± 8.2% after 138 days of storage. The study authors indicated that these results supported stability for the period of storage during the study.

Filter paper application monitoring samples were folded, placed into pre-labeled 500 mL wide-mouth HDPE amber bottles, capped and sealed with electrical tape, and placed in an insulated container with ice packs until they could be placed into a storage freezer (pp. 19-20). The samples were kept separate from all other samples to prevent contamination. The maximum storage period for filter papers was 133 days (Appendix 14, p. 279). No separate freezer storage and transit stability studies were performed for filter paper samples.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Each primary sampling unit consisted of a polyurethane foam (PUF) sorbent tube (SKC Catalog Number 226-92) connected with Tygon tubing to an SKC® personal air sampling pump with a flow rate of 3 L/min (Model Number 224-52; p. 20). Each secondary sampling unit consisted of an XAD-2 OVS sorbent tube (SKC Catalog Number 226-30-16) connected with Tygon tubing to an air sampling pump with a flow rate of 1 L/min. Secondary samples were never analyzed (p. 23). Vapor collection tubes were covered with a plastic PVC pipe to protect them from sunlight. The flow for each sampler was calibrated at the start of each monitoring period using a Bios International Defender flow meter.

- Extraction method: The contents of the PUF sorbent tubes were removed by pushing forward from the air-hose end with a glass transfer pipette or by gently pulling the sorbent with forceps into a 50 mL polypropylene centrifuge tube (Appendix 14, p. 275). The sample was extracted using 40 mL of acetone-with-1% v/v-formic-acid by shaking horizontally for 30 minutes (*ca.* 300 cycles per minute) and then ultra-sonicating for 10 minutes. The contents were allowed to settle. An aliquot was transferred to a glass culture tube. The sample was fortified with internal standard, evaporated to near dryness, and reconstituted with 0.5 mL of 5:95 Methanol:Water with 0.1% formic acid. Additional dilutions for high concentrations samples were performed using acetone-with-1% v/v-formic acid before the addition of internal standard. A final fraction was transferred to a LC autosampler vial and analyzed using NCI LC-MS/MS with electrospray ionization in negative ion mode (Appendix 14, p. 346).

- Method validation (Including LOD and LOQ): Method verification of Syngenta Method GRM022.08A was achieved by analysis of three replicates each of blank untreated control PUF sorbent tubes fortified with 0.5 ng, 1.0 ng, 2.0 ng, and 10 ng of dicamba (Appendix 14, pp. 271, 276, 284). These data supported a limit of quantitation of 1 ng/sample, the lowest fortification level at which acceptable recovery was demonstrated. The limit of detection was determined to be 0.5 ng due to background noise making results less reliable at that level. Accuracy was within 70-120% and precision was ≤20% RSD at all fortification levels tested. The ECM and ILV for this method are presented in MRIDs 50102120 and 50102121, which were assessed in a separate DER.

- Instrument performance: Calibration standards were prepared at 0.1, 0.5, 1, 2, 10, 40, and 80 ng per sorbent tube (Appendix 14, p. 274). Calibration standards and samples were analyzed using LC-MS/MS (Appendix 14, p. 278). Calibration curves and residue values were

calculated using LCQuan 2.5 data handling software using linear regression with 1/x weighting. The relative response of the LC-MS/MS to dicamba was linear over a range of 0.1 ng to 80 ng.

8. Quality Control for Air Sampling

Lab Recovery: More than half of the laboratory spike recoveries are within the acceptable range of 90-110% following fortification at 0.5, 1, 2, 10, 100, and 1,000 ng (Appendix 14, Table 2, p. 285). 24 of 53 recoveries were outside the acceptable range. Recoveries outside the acceptable range included all three samples at 0.5 ng with percent recoveries of 83, 81, and 74; 5 of 8 samples at 1 ng with percent recoveries of 85, 81, 85, 80, and 74; 2 of 3 samples at 2 ng with percent recoveries of 85 and 89; 7 of 17 samples at 10 ng with percent recoveries of 153, 189, 88, 75, 71, 71, and 86; 1 of 4 samples at 100 ng with a percent recovery of 89; and 6 of 18 samples at 1,000 ng with percent recoveries of 114, 119, 117, 112, 146, and 154.

Field blanks: Dicamba was detected in two of three pre-application PUF samples collected at Plot FV1, at 2.41 ng and 0.562 ng (Appendix 14, Table 5, p. 292). Dicamba was not detected in two pre-application samples collected from Plot FV2 (Appendix 14, Table 5, p. 296).

Field Recovery: Field spike recoveries are within the acceptable range for tubes spiked with 1000 and 10,000 ng, with overall recoveries between 92 and 103% (Appendix 14, p. 280; Table 6, p. 299). However, spike samples at the 1 ng fortification level had recoveries of 1,066% and 473%, and a 24-hour control sample had dicamba residues of 1.86 ng. Study authors speculated that these exceptionally high results were due to contamination.

Travel Recovery: One set of transit stability samples was prepared, consisting of three replicate spiked samples at a fortification level of 1,000 ng and two control samples (Appendix 14, p. 281 and Appendix 14, Table 8, p. 301). Dicamba was not detected in the two control samples and was detected at 83%, 98%, and 92% in the three spiked samples.

Breakthrough: Samples that were fortified at 1 µg and 10 µg (1,000 and 10,000 ng) per tube showed average recoveries of 102% and 98%, respectively (pp. 22, 30; Appendix 14, p. 280). The highest dicamba amount measured on a PUF sample was 11.9 ng (Appendix 14, Table 5, pp. 292-298) which is *ca.* 0.1% of the highest fortification (10,000 ng). This indicates that dicamba loss due to breakthrough is unlikely.

9. Application Verification

To verify the application of the test substance, ten pre-labeled pans, each containing five 12.5 cm diameter Whatman #3 filter papers were placed at random locations in the treated soybean plot (pp. 19-20). After application, the applied substance was allowed to dry, the pans were collected from the field, and filter papers were folded and placed into a pre-labeled 500 mL wide-mouth HDPE amber bottle. The bottles were sealed and cooled with ice packs until they could be placed into a storage freezer.

Overall application monitoring results at the FV1 application were within 6.59% of the theoretical value, and within 0.95% at the FV2 application (p. 29). Individual sample variance at FV1 ranged from -11.02% to +32.19%. Individual sample variance at FV2 ranged from -5.6% to 11.29%. Recovery achieved on extraction and analysis of field spikes was 98% ± 9.5% (RSD) with a range of 79% to 121% (p. 30).

10. Deposition and Air Concentration Modeling

The study authors used the flux rates derived from the field study and AERMOD to evaluate air concentrations and deposition from a 10-acre, treated soybean field. Two pre-processors, AERMET and AERMAP, were used to derive inputs for the AERMOD modelling system. AERMET was used to process the atmospheric boundary layer parameters from meteorological observations and derive friction velocity, Monin-Obukhov length, convective velocity, potential temperature, mixing height and surface heat flux. AERSURFACE was used to generate the surface characteristics (albedo, surface roughness and Bowen ratio) for AERMET. Terrain data was extracted and processed by AERMAP for gridded or discrete receptors.

Hourly surface observations were retrieved from York Municipality Airport (WBAN 14989) from the National Climatic Data Centre (NCDC) available at http://www.noaa.gov/ while upper air meteorological observations were retrieved from the National Weather Station (NWS) Omaha/Valley, NE weather station (WBAN 94980). One-year (2016) weather data was supplied to the dispersion model, however dicamba deposition and air concentration were only analyzed during the study periods (FV1: July 12 – 16, FV2: July 14 – 21).

Modeling estimates of upper-bound 90th percentile total dicamba deposition (wet plus dry deposition) at 5 m from the edge of the treated field for the 24-hour averaging period ranged from 6.73×10^{-7} to 7.22×10^{-6} lb/A for Field 2 and 4.61×10^{-7} to 5.96×10^{-6} lb/A for Field 1. The highest 24-hour average air concentration from modeling was 1.75 ng/m^3 for Field 1 and 0.86 ng/m^3 for Field 2.

The reviewer did not confirm these modeling estimates, as EPA typically evaluates air concentrations and deposition from an 80-acre field using PERFUM and AERMOD, respectively.

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

Indirect Method

The indirect method, commonly referred to as the "back calculation" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information are used in combination with the ISCST3 dispersion model (Version 02035) and a unit flux rate of 0.001 $\mu g/m^2 \cdot s$ to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the ISC model runs are compared to those concentrations actually measured, and a regression is performed, using the modeled values along the x-axis and the measured values along the y-axis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson et al., 1999.

Aerodynamic Method

The aerodynamic method, also referred to as the "flux-gradient" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation, which is shown in the following expression:

Equation 1

$$P = \frac{k^2(\Delta\bar{c})(\Delta\bar{u})}{\phi_m \phi_p [\ln\left(\frac{z_2}{z_1}\right)]^2}$$

where P is the flux in units of $\mu g/m^2 \cdot s$, k is the von Karman's constant (dimensionless ~0.4), $\Delta\bar{c}$ is the vertical gradient pesticide residue concentration in air in units of $\mu g/m^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta\bar{u}$ is the vertical gradient wind speed in units of m/s between heights z_{top} and z_{bottom}, and ϕ_m and ϕ_p are the momentum and vapor stability correction terms respectively. Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind

shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into Equation 1 to arrive at Equation 2 which is ultimately used to compute the flux.

Equation 2

$$Flux = \frac{-(0.42)^2 (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

where ϕ_m and ϕ_p are internal boundary layer (IBL)stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

Equation 3

$$R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + \left(u_{ztop} - u_{zbottom}\right)^2}$$

where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if $R_i > 0$ (for Stagnant/Stable IBL)

$\phi_m = (1 + 16R_i)^{0.33}$ and $\phi_p = 0.885(1 + 34R_i)^{0.4}$

if $R_i < 0$ (for Convective/Unstable IBL)

$\phi_m = (1 - 16R_i)^{-0.33}$ and $\phi_p = 0.885(1 - 22R_i)^{-0.4}$

The minimum fetch requirement, that the fetch is 100 times the highest height of the air sampler (1.5 m) for this method to be valid, was not satisfied for either field. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the "mass balance" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the integrated horizontal flux method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from ca. 0.5 to 5 feet. Likewise, wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log law relationships for the atmospheric boundary layer. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux method is the following expression:

Equation 4

$$P = \frac{1}{x} \int_{Z_0}^{Z_p} \bar{c}\bar{u} dz$$

where P is the volatile flux in units of µg/m^2·s, $\bar{c}$ is the average pesticide residue concentration in units of µg/m^3 at height Z in units of meters, $\bar{u}$ is the wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top in units of meters, and dz is the depth of an incremental layer in units of meters. Following trapezoidal integration, equation 3 is simplified as follows in equation 5 (Yates, 1996):

Equation 5

$$P = \frac{1}{x}\sum_{Z_0}^{Z_P}(A * Ln(z) + B) * (C * Ln(z) + D)dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), z is the height above ground level. Z_p can be determined from the following equation:

Equation 6

$$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$

The minimum fetch requirement of 20 meters for this method to be valid was satisfied for both fields. Soybeans were planted on both fields on June 1, 2016. The broadcast applications were made to the plots on July 12 and 14, 2016 (41 and 43 days after planting). The height of the soybean plants at the time of application were not specified, but the plants were characterized as being in the R1 growth stage. It is unclear whether the maximum surface roughness length requirement of 0.1 meters for the method to be valid was satisfied.

B. Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Tables 5 and 6**.

Table 5. Field volatilization flux rates of dicamba obtained in study at plot FV1.

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($ng/m^2/sec$)	Registrant ($ng/m^2/sec$)	Empirical Flux Determination Method	Notes
Application	7/12/16 8:44 – 9:24	0.683	2.40	2.40	ID	
1	7/12/16 9:24 – 13:00	3.60	0.041	0.04027	IHF	A
2	7/12/16 13:00 – 19:00	6.00	0.240	0.25183	IHF	
3	7/12-13/16 19:00 – 1:00	6.00	0.038	0.03806	IHF	
4	7/13/16 1:00 – 7:00	6.00	0.572	0.64216	IHF	A
5	7/13/16 7:00 – 20:00	13.0	0.084	0.20730	IHF	A
6	7/13-14/16 20:00 – 7:00	11.0	0.004	0.00403	IHF	
7	7/14/16 7:00 – 20:00	13.0	0.044	0.05392	IHF	
8	7/14-15/16 20:00 – 7:00	11.0	0.005	0.00304	IHF	
9	7/15/16 7:00 – 20:00	13.0	0.058	0.03149	IHF	A
10	7/15-16/16 20:00 – 7:00	11.0	Not calculated	Not calculated	IHF	B
11	7/16/16 7:00 – 20:00	13.0	0.002	0.04312	IHF	
12	7/16-17/16 20:00 – 7:00	11.0	Not calculated	Not calculated	IHF	B
13	7/17/16 7:00 – 20:00	13.0	Not calculated	Not calculated	IHF	B
14	7/17-18/16 20:00 – 20:00	24.0	Not calculated	Not calculated	IHF	B
15	7/18-19/16 20:00 – 20:00	24.0	Not calculated	Not calculated	IHF	B

Data obtained from Tables 1-3, pp. 39-41 and Table 13, p. 51 in the study report and the accompanying Excel spreadsheets.

*Methods legend: ID = Indirect method, IHF = Integrated Horizontal Flux.

Notes

A Reviewer removed data points from the regression analysis to provide a better fit

B Dicamba was not detected or was detected at only one or two sample heights. No flux was calculated by the registrant or reviewer.

Table 6. Field volatilization flux rates of dicamba obtained in study at plot FV2.

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($ng/m^2/sec$)	Registrant ($ng/m^2/sec$)	Empirical Flux Determination Method	Notes
Application	7/14/16 10:25 – 11:02	0.633	5.10	5.10	ID	
1	7/14/16 11:02 – 13:00	1.97	1.013	1.22341	IHF	A
2	7/14/16 13:00 – 19:00	6.00	0.075	0.08342	IHF	
3	7/14-15/16 19:00 – 1:00	6.00	0.040	0.04350	IHF	
4	7/15/16 1:00 – 7:00	6.00	0.015	0.00006	IHF	A
5	7/15/16 7:00 – 20:00	13.0	0.048	0.04806	IHF	
6	7/15-16/16 20:00 – 7:00	11.0	Not calculated	Not calculated	IHF	B
7	7/16/16 7:00 – 20:00	13.0	0.139	0.25271	IHF	C
8	7/16-17/16 20:00 – 7:00	11.0	Not calculated	Not calculated	IHF	B
9	7/17/16 7:00 – 20:00	13.0	0.027	0.05025	IHF	
10	7/17-18/16 20:00 – 7:00	11.0	0.03	Not calculated	IHF	B
11	7/18/16 7:00 – 20:00	13.0	Not calculated	Not calculated	IHF	B
12	7/18-19/16 20:00 – 7:00	11.0	Not calculated	Not calculated	IHF	B
13	7/19/16 7:00 – 20:00	13.0	Not calculated	Not calculated	IHF	B
14	7/19-20/16 20:00 – 20:00	24.0	0.009	0.00985	IHF	
15	7/20-21/16 20:00 – 20:00	24.0	0.035	0.00002	IHF	

Data obtained from Tables 4-6, pp. 42-44 and Table 13, p. 51 in the study report and the accompanying Excel spreadsheets.

*Methods legend: ID = Indirect method, IHF = Integrated Horizontal Flux.

Notes

A Reviewer removed data points from the regression analysis to provide a better fit

B Dicamba was not detected or was detected at only one or two sample heights. No flux was calculated.

C Low r-squared value for concentration regression .

Under field conditions at Plot FV1, based on calculations using the Integrated Horizontal Flux method, dicamba had a peak volatile flux rate of 0.572 ng/m^2·s accounting for 0.022% of the applied mass observed 15.6 to 21.6 hours post-application. By the end of the study, a total of 0.05% of dicamba volatilized and was lost from the field. Observed flux rates were diurnal and generally highest during daytime periods of high temperatures, except for the highest flux rate which occurred between 1 and 7 am.

Under field conditions at Plot FV2, based on calculations using the Integrated Horizontal Flux method, dicamba had a peak volatile flux rate of 1.01 ng/m^2·s accounting for 0.0128% of the applied mass observed 0 to 1.97 hours post-application. By the end of the study, a total of 0.045% of dicamba volatilized and was lost from the field. Observed flux rates were diurnal and generally highest during daytime periods of high temperatures.

III. Study Deficiencies and Reviewer's Comments

1. The registrant used a different approach to calculate Z_p, the top of the concentration plume, than that recommended by EPA when calculating volatilization flux rates using the Integrated Horizontal Flux method. The registrant used:

$$Z_p = \exp\left(\frac{-D}{C}\right)$$

   C and D are the slope and intercept of the log-linear concentration regression. This results in differences between flux values calculated in the registrant report and in the reviewer spreadsheets.

2. Dicamba was detected in two of three pre-application samples collected from Plot FV1.

3. Dicamba concentrations did not always decrease with height during sampling periods. As a result, in order to achieve better regressions, some sampling points were excluded when determining the log-linear vertical profiles for concentration. It should be noted that in most cases where this occurred, amounts of dicamba in the samplers were equal to or less than 2 ng/PUF. Lab recoveries for samples at or below 2 ng/PUF showed recoveries typically below 90%. Additionally, the two field recoveries at 1ng/PUF showed unacceptable recoveries. As such, there is uncertainty that the analytical method was sufficient to accurately measure dicamba in the PUFs. However, as the lower air measurements (*i.e.*, 2 ng/sample) are associated with lower concentrations and associated flux calculations, and as the higher measurements are considered reliable, the poor recovery issues should not significantly impact the use of the derived flux calculations in air modeling.

4. Temperatures during the conduct of the trials did not exceed 90°F. Average temperatures for the first three days of each trial were in the 70s. As such, it is unclear if the estimated flux rates are considered conservative and protective of what could occur.

5. The ECM and ILV for air sampling method GRM022.08A are presented in MRIDs 50102120 and 50102121, respectively, which were assessed in a separate DER. In the ECM, no samples were prepared at 10×LOQ for the filter paper matrix. In the ILV, linearity was

not satisfactory. The specificity of the method for the air sampling tubes was not supported by the representative chromatograms of the ECM and/or ILV.

6. Soil bulk density and organic matter content were reported at only a single depth of 0-6 inches.

7. Meteorological data were sampled at a frequency of 1 minute, but only one-hour averages were reported in the study and provided for use in the estimation of flux.

IV. References

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

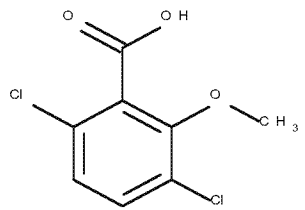
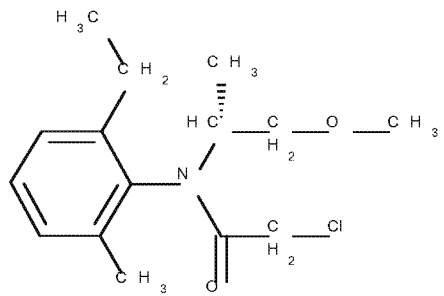
Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. Environmental Science and Technology, 24:1490-1497.

Syngenta Method GRM022.08A (DRAFT). "Dicamba – Method GRM022.08A for the Determination of Dicamba from Air Sampling Tube and Filter Paper by LC-MS/MS", Syngenta Crop Protection, LLC. Greensboro, NC USA.

Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

DER ATTACHMENT 1. Dicamba + s-metolachlor and Its Environmental Transformation Products. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
A21472C (Dicamba + s-metolachlor)	**Dicamba** **IUPAC:** 3,6-Dichloro-o-anisic acid **CAS:** 3,6-Dichloro-2-methoxybenzoic acid **CAS No.:** 1918-00-9 **Formula:** $C_8H_6Cl_2O_3$ **MW:** 221.04 g/mol **SMILES:** COc1c(Cl)ccc(Cl)c1C(O)=O		835.8100 Field volatility	50102118	NA	NA
	S-metolachlor **IUPAC:** 2-Chloro-N-(6-ethyl-o-tolyl)-N-[(1S)-2-methoxy-1-methylethyl]acetamide **CAS:** 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]acetamide **CAS No.:** 87392-12-9 **Formula:** $C_{15}H_{22}ClNO_2$ **MW:** 283.8 g/mol **SMILES:** Cc1cccc(CC)c1N(C(=O)CCl)C(C)COC					

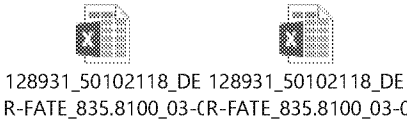
Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

[A] AR means "applied radioactivity". MW means "molecular weight". NA means "not applicable".

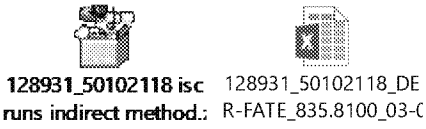
DER Attachment 2: Statistics Spreadsheets and Graphs

The electronic spreadsheet files are inserted below for calculations using the Integrated Horizontal Flux Method and the Indirect Method for determination of the emission rate of dicamba after application in the formulation A21472C Herbicide with VaporGrip™ Technology.

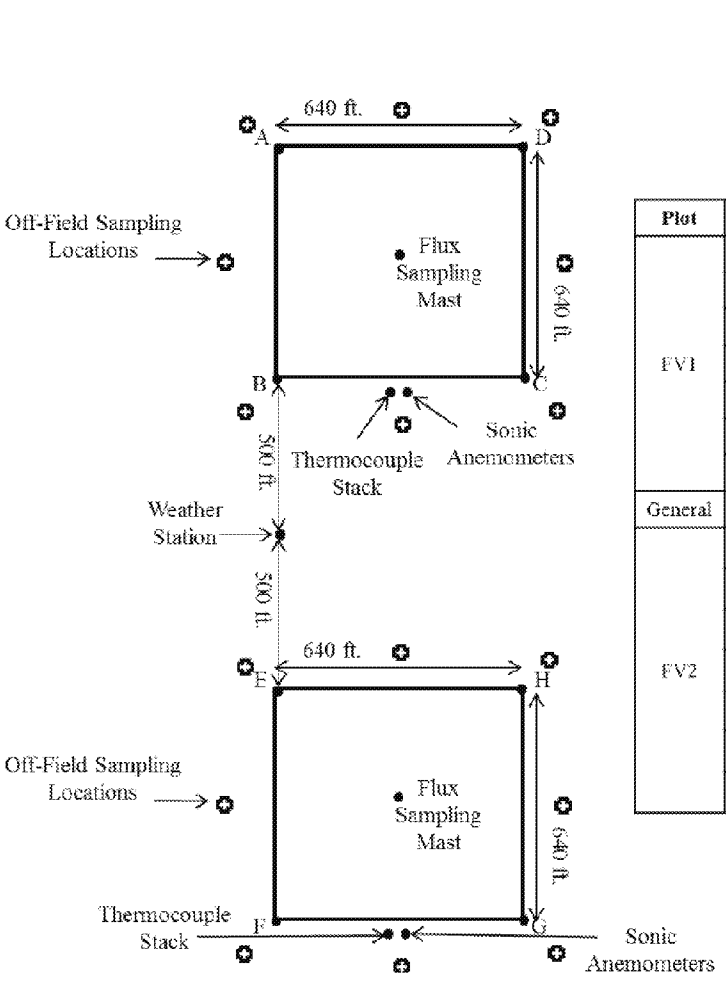
1. Validation spreadsheet for studies following the Integrated Horizontal Flux Method for Plots FV1 and FV2:



2. ISC modeling files and validation spreadsheet for studies following the Indirect Method for Plots FV1 and FV2:



DER Attachment 3: Field Volatility Study Design and Plot Maps



Slope (0-1%)

Plot	Point	Latitude (°N)	Longitude (°W)
FV1	A	40.9086373	-97.68312523
	B	40.90688724	-97.68311808
	C	40.90685433	-97.68077218
	D	40.90860798	-97.68077581
	Flux Mast	40.90774618	-97.68196529
	Wind Speed	40.90682770	-97.68189405
	Thermocouple Sensors	40.90682898	-97.68201075
General	Weather Station	40.90526079	-97.68316217
FV2	E	40.90426209	-97.68309669
	F	40.90251231	-97.68309544
	G	40.90248029	-97.68076646
	H	40.90423109	-97.68077104
	Flux Mast	40.90337095	-97.68193527
	Wind Speed	40.90247962	-97.68269057
	Thermocouple Sensors	40.90248213	-97.68279997

This figure not drawn to scale.

Figure obtained from Figure 9, p. 61, of the study report.